Relative Lewis Basicities of Six $Al(OR_F)_4^-$ Superweak Anions and the Structures of $LiAl\{OCH(CF_3)_2\}_4$ and $[1\text{-Et-3-Me-1,3-}C_3H_3N_2]$-$[Li\{Al\{OCH(CF_3)_2\}_4\}_2]$

Svetlana M. Ivanova, Benjamin G. Nolan, Yoshihiro Kobayashi, Susie M. Miller, Oren P. Anderson, and Steven H. Strauss*[a]

Abstract: The relative Lewis basicities of six $Al(OR_F)_4^-$ ions, $Al\{OC(CH_3)(CF_3)_2\}_4^-$, $Al\{OC(CF_3)_3\}_4^-$, $Al\{OCPh(CF_3)_2\}_4^-$, $Al\{OC\{4\text{-}C_6H_4(t\text{Bu})\}(CF_3)_2\}_4^-$, $Al\{OC(Cy)(CF_3)_2\}_4^-$, and $Al\{OCPh_2(CF_3)\}_4^-$, have been determined by measuring their relative coordinating abilities towards Li^+ in dichloromethane. The relative Li^+ Lewis basicities of the $Al(OR_F)_4^-$ ions are linearly related to the aqueous pK_a values of the corresponding parent HOR_F fluoroalcohols. The Lewis basicity of $Al\{OCH(CF_3)_2\}_4^-$ could not be measured because two of these anions can coordinate to one Li^+ cation. The structures of $LiAl\{OCH(CF_3)_2\}_4$ and $[1\text{-Et-3-Me-1,3-}C_3H_3N_2][Li\{Al\{OCH(CF_3)_2\}_4\}_2]$ were determined.

Keywords: alkoxides · aluminum · basicity · Lewis acids · lithium

Introduction

The synthesis and applications of superweak anions[1, 2] that are thermally, chemically, and electrochemically robust has been an active endeavor in many laboratories during the past decade.[2, 3] One relatively new class of superweak anions is based on monodentate polyfluoroalkoxide and -aryloxide substituents and includes $B\{OCH(CF_3)_2\}_4^-$,[4] $Al\{OCR(CF_3)_2\}_4^-$ (R = H,[5–9] CH_3,[5–9] Cy,[8, 9] Ph,[5, 7–9] $4\text{-}C_6H_4CH_3$,[8, 9] $4\text{-}C_6H_4(t\text{Bu})$,[8, 9] CF_3,[4, 5, 8, 9]) $Al\{OCPh_2(CF_3)\}_4^-$,[8, 9] $Al(OC_6F_5)_4^-$,[11] $Nb(OC_6F_5)_6^-$,[11] and $Nb\{OCH(CF_3)_2\}_6^-$.[12] The lithium salt of the $Al\{OCPh(CF_3)_2\}_4^-$ ion is an active Lewis acid catalyst in toluene for the 1,4-conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyls and for the direct substitution of allylic acetates by silyl ketene acetals.[10] In addition, a solution of $LiAl\{OC(CF_3)_3\}_4$ in 1,2-dimethoxyethane (DME; 0.01 M) has a direct current (dc) conductivity that is nearly 100 times higher than a solution of $LiCF_3SO_3$ in DME (0.01 M).[13]

We are investigating the relative Lewis basicities of $Al(OR_F)_4^-$ superweak ions and the relative Lewis acidities of $LiAl(OR_F)_4$ compounds. In this paper, we report the relative Lewis basicities of six $Al(OR_F)_4^-$ ions, $Al(hftb)_4^-$, $Al(pftb)_4^-$, $Al(hfpp)_4^-$, $Al(hfBupp)_4^-$, $Al(hfcp)_4^-$, and $Al(dpte)_4^-$ ($HFTB^- = OC(CH_3)(CF_3)_2^-$; $PFTB^- = OC(CF_3)_3^-$; $HFPP^- = OCPh(CF_3)_2^-$; $HFBuPP^- = OC\{4\text{-}C_6H_4(t\text{Bu})\}(CF_3)_2^-$; $HFCP^- = OC(Cy)(CF_3)_2^-$; $DPTE^- = OCPh_2(CF_3)^-$). The measurement of the relative Lewis basicity of $Al(hfip)_4^-$ was not possible because, unlike the other six $Al(OR_F)_4^-$ examined in this study, two $Al(hfip)_4^-$ can simultaneously coordinate to one Li^+ cation ($HFIP^- = OCH(CF_3)_2^-$). In the course of investigating this anomaly, the structures of $LiAl(hfip)_4$ and $[EMI][Li\{Al(hfip)_4\}_2]$ were determined ($EMI^+ = 1\text{-Et-3-Me-1,3-}C_3H_3N_2^+$).

Experimental Section

Materials and reagents: All preparations and physical measurements were carried out with rigorous exclusion of air and water. Schlenk or glovebox techniques were employed, with purified nitrogen, helium, or argon used when an inert atmosphere was required. All reagents and solvents were reagent grade or better. The compounds $N(n\text{Bu})_4Cl$ (Aldrich, ≥99%) and [EMI]Cl (Aldrich, ≥98%) were used as received. The compound $LiAlH_4$ (Aldrich) was recrystallized from diethyl ether and stored in a Vacuum Atmospheres glovebox. The polyfluoroalcohols H(HFIP), H(HFPP) (Central Glass), H(HFTB) (Fluorochem USA), and H(PFTB) (Fluorochem USA) were dried over activated 4 Å molecular sieves and vacuum distilled. The polyfluoroalcohols H(HFCP), H(DPTE), and H(HFBuPP) were prepared and dried by literature procedures.[8] Distilled water was purified and deionized (to 18 MΩ) with a Barnstead Nanopure purification system. The following solvents were purified by distillation under nitrogen or under vacuum from the indicated drying agent: benzene (Na); hexanes (Na); diethyl ether (Na); $1,1,2\text{-}C_2Cl_3F_3$ (P_2O_5); acetonitrile (P_2O_5); dimethylsulfoxide (activated 13X molecular sieves); dichloromethane

---

[a] Prof. S. H. Strauss, Dr. S. M. Ivanova, B. G. Nolan, Y. Kobayashi,
S. M. Miller, Prof. O. P. Anderson
Department of Chemistry, Colorado State University
Ft. Collins, CO 80523 (USA)
Fax: (+1) 970-491-1801
E-mail: strauss@chem.colostate.edu

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author. Figure S-1, Figure S-2, and Figure S-3 are crystallographic numbering schemes for $[EMI][Li(Al(hfip)_4)_2]$ and $LiAl(hfip)_4$. Figure S-4 and Figure S-5 are ^1H NMR spectra. Table S-1 lists bond valence parameters.

0947-6539/01/0702-0503 $ 17.50+.50/0

(P_2O_5); [D$_2$]dichloromethane (Cambridge, >99% D; P_2O_5), hexafluorobenzene (P_2O_5). The compounds LiAl(hftb)$_4$, LiAl(pftb)$_4$, LiAl(hfpp)$_4$, LiAl(hfBupp)$_4$, LiAl(hfcp)$_4$, and LiAl(dpte)$_4$ were prepared by literature procedures.[5–8]

Preparation of LiAl(hfip)$_4$: The compound LiAl(hfip)$_4$ was prepared by treating a suspension of $LiAlH_4$ (0.552 g, 14.5 mmol) in 1,1,2-$C_2Cl_3F_3$ (100 mL) at 0 °C with a solution of $HOCH(CF_3)_2$ (12.2 g, 72.6 mmol) in 1,1,2-$C_2Cl_3F_3$ (20 mL). The solution was added dropwise over 10 min and was vigorously stirred at 0 °C for 18 h and at 25 °C for an additional six days. After this time, all volatiles were removed under vacuum from the reaction mixture, leaving 9.6 g of the white microcrystalline compound LiAl(hfip)$_4$ (94% yield). NMR spectral data for this compound are listed in Table 1. The purity of the compound, ≥99%, was judged by the absence of ^{1}H and ^{19}F NMR resonances and mass spectral peaks due to likely impurities such as $AlH_n(hfip)_{4-n}^-$ ($n = 1,2,3$), $AlF(hfip)_3^-$, and $Al(OH)(hfip)_3^-$.

Preparation of [EMI][Al(hfip)$_4$]: The compound [EMI][Al(hfip)$_4$] was prepared by mixing LiAl(hfip)$_4$ (0.101 g, 0.143 mmol) and [EMI]Cl (0.021 g, 0.14 mmol) in dichloromethane (20 mL) for 18 h at 25 °C. The resulting suspension was filtered through Celite and solvent was removed under vacuum, leaving 0.094 g of the white microcrystalline solid [EMI][Al(hfip)$_4$] (82% yield). NMR spectral data for this compound are listed in Table 1.

Preparation of [N(*n*Bu)$_4$][Al(OR$_F$)$_4$]: The compounds [N(*n*Bu)$_4$][Al(OR$_F$)$_4$] were prepared by mixing any one of six LiAl(OR$_F$)$_4$ compounds with an equimolar amount of N(*n*Bu)$_4$Cl in dichloromethane. Of the seven LiAl(OR$_F$)$_4$ compounds used in this study, only LiAl(hfBupp)$_4$ was not converted to the $N(nBu)_4^+$ salt. The resulting suspensions (LiCl is not soluble in dichloromethane) were filtered through Celite and solvent was removed under vacuum, leaving white microcrystalline solids. In a typical reaction, LiAl(hfpp)$_4$ (0.200 g, 0.199 mmol) and N(*n*Bu)$_4$Cl (0.055g, 0.199 mmol) were stirred in dichloromethane for 24 h at 25 °C. After filtration and vacuum drying for 4 h, 0.23 g of the white microcrystalline solid [N(*n*Bu)$_4$][Al(hfpp)$_4$] was isolated (95% yield). A ^{7}Li NMR spectrum of the solid did not show the presence of unreacted LiAl(hfpp)$_4$. The signal/noise ratio of this NMR experiment limits the amount of undetected LiAl(hfpp)$_4$ in the sample of [N(*n*Bu)$_4$][Al(hfpp)$_4$] to ≤1%. NMR spectral data for this compound and for the other five [N(*n*Bu)$_4$][Al(OR$_F$)$_4$] compounds that were prepared are listed in Table 1.

Physical measurements: NMR spectra were recorded by using a Varian Inova-300 spectrometer operating at the indicated frequencies and with the indicated chemical shift standards: ^{1}H, 300.1 MHz, internal $CHDCl_2$ ($\delta = 5.32$); ^{7}Li, 116.6 MHz, external 1M aqueous $LiNO_3$ ($\delta = 0$); ^{19}F, 282.4 MHz, internal C_6F_6 ($\delta = = -162.59$). Negative-ion electrospray mass spectra were recorded using a Fisons VG Quattro-SQ mass spectrometer with a cone voltage of 20 V.

Table 1. ^{1}H, ^{7}Li, and ^{19}F NMR data for $Al(OR_F)_4^-$ ions.[a]

	$\delta(^1H)$	$\delta(^7Li)$	$\delta(^{19}F)$
LiAl(hfip)$_4$	4.54 (sp, $J_{HF} = 5.6$ Hz)	−1.34	−76.93
[TBA][Al(hfip)$_4$]	4.49 (sp, $J_{HF} = 5.6$ Hz)		−77.26
[EMI][Al(hfip)$_4$]	4.58 (sp, $J_{HF} = 5.9$ Hz)		
LiAl(hftb)$_4$	1.50	−1.38	−79.77
[TBA][Al(hftb)$_4$]		1.50	−79.83
LiAl(pftb)$_4$		[b]	−75.22
[TBA][Al(pftb)$_4$]			−75.64
LiAl(hfcp)$_4$	[c]	−1.14	−72.51
[TBA][Al(hfcp)$_4$]		[c]	−72.07
LiAl(hfpp)$_4$	7.71(d), 7.39(m), 7.22(m)	−0.80	−75.30
[TBA][Al(hfpp)$_4$]	7.76(d), 7.32(m), 7.18(m)		−74.70
LiAl(dpte)$_4$	7.26(m), 7.08(m)	−1.42	−72.61
[TBA][Al(dpte)$_4$]	7.26(d), 7.12(m), 6.99(m)		−72.35
LiAl(hfBupp)$_4$	7.65(d), 7.25(d), 1.25	−0.82	−75.32

[a] All spectra recorded in [D$_2$]dichloromethane at 25 °C. All resonances were singlets or unresolved multiplets unless otherwise indicated. HFIP = $OCH(CF_3)_2$, HFTB = $OC(CH_3)(CF_3)_2$, PFTB = $OC(CF_3)_3$, HFCP = $OC(Cy)(CF_3)_2$, HFPP = $OCPh(CF_3)_2$, DPTE = $OCPh_2(CF_3)$, HFBuPP = $OC(4\text{-}C_6H_4(tBu))(CF_3)_2$, TBA$^+$ = $N(nBu)_4^+$, EMI$^+$ = 1-Et-3-Me-1,3-$C_3H_3N_2^+$, sp = septet, d = doublet, m = second-order multiplet. [b] This $\delta(^7Li)$ value could not be determined because LiAl(pftb)$_4$ is only sparingly soluble in [D$_2$]dichloromethane. [c] This NMR spectrum is included in the Supporting Information.

Determination of acid dissociation constants: Acid dissociation constants (pK_a values) of the polyfluoroalcohols H(PFTB), H(HFPP) and H(HFCP) were determined by potentiometric titration in water with 0.1M NaOH using an Orion model 720A pH meter and an Orion Ross hydrogen-ion electrode. Our measured pK_a value for H(PFTB), 5.4, is in agreement with the literature value.[14] Our measured pK_a values for H(HFPP) and H(HFCP) are 8.8 and 10.3, respectively. The pK_a values for H(HFIP) and H(HFTB), 9.3 and 9.6, respectively, were taken from the literature.[14] No recognizable end point was observed in the titration of H(DPTE). The low aqueous solubility of H(HFBuPP) prevented the measurement of its pK_a value in water. Instead, the apparent pK_a value in 60:40 (*v*/*v*) DMSO/H_2O was determined as described in the literature (DMSO = dimethylsulfoxide).[15] A plot of 60:40 (*v*/*v*) DMSO/H_2O pK_a values versus aqueous pK_a values for several fluoroalcohols is shown in Figure 1. Using this method, we determined the aqueous pK_a value of H(HFBuPP) to be 9.3.

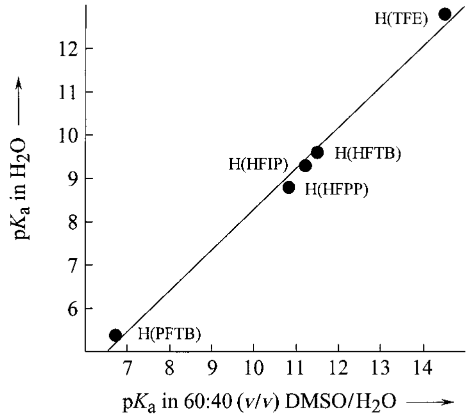


Figure 1. Plot of aqueous vs 60:40 (*v*/*v*) DMSO/H_2O pK_a values. The straight line is a linear least-squares fit to the data. Abbreviations: H(PFTB) = $HOC(CF_3)_3$; H(HFPP) = $HOCPh(CF_3)_2$; H(HFIP) = $HOCH(CF_3)_2$; H(HFTB) = $HOCMe(CF_3)_2$; H(TFE) = $HOCH_2CF_3$.

Conductivity measurements: Solution conductivities were measured at 25 °C in a helium-filled Vacuum Atmospheres glovebox with a Yellow Springs Instrument Model 31A conductance bridge and a Model 3403 cell that was calibrated for inverted use (cell constant $k = 0.998\ \text{cm}^{-1}$). Solutions were prepared in the glovebox by adding acetonitrile to weighed samples in 3 mL volumetric flasks. The conductivity of the acetonitrile used was determined to be less than or equal to 1 μS cm^{-1}. The variations in conductivity for a given compound for replicate samples for a given batch of compound and for different batches of compound were no more than ±2%.

X-ray crystallography: Crystals of LiAl(hfip)$_4$ were grown from a 10:1 (*v*/*v*) solution of benzene and hexafluorobenzene at 25 °C. Crystals of [EMI][Li{Al(hfip)$_4$}$_2$] were grown by slow diffusion of hexanes into a saturated dichloromethane solution of an equimolar mixture of [EMI][Al(hfip)$_4$] and Li(Al(hfip)$_4$ at 25 °C. In both cases, a suitable crystal was examined under an argon atmosphere and was placed in the cold nitrogen stream of the low-temperature LT-2 unit of a Siemens SMART CCD diffractometer system. The diffraction data collection and subsequent structural computations were performed using the crystallographic software supplied by Siemens[16] or by Professor G. M. Sheldrick.[17] Lorentz and polarization corrections were applied to the data. Details of the crystallographic experiments and subsequent computations are listed in Table 2.[18, 19] The structures were solved by direct methods and were refined using full-matrix least-squares procedures on F^2 for all data. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Selected interatomic bond lengths and angles are listed in Table 3 and Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145394 (EMI^+ salt) and CCDC-145395 ($LiAl(hfip)_4$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Details of the X-ray diffraction study of $LiAl(hfip)_4$ and $[EMI][Li\{Al(hfip)_4\}_2]$.[a]

	$LiAl(hfip)_4$	$[EMI][Li\{Al(hfip)_4\}_2]$
formula	$C_{12}H_4AlF_{24}LiO_4$	$C_{30}H_{19}Al_2F_{48}LiN_2O_8$
M_w [g mol^{-1}]	702.07	1508.37
T [K]	170	169
space group	$P1$	$P2_1/c$
a [Å]	10.1184(7)	14.5455(1)
b [Å]	10.5213(7)	48.3469(8)
c [Å]	11.6461(8)	16.5474(2)
α [°]	76.587(1)	90.000
β [°]	80.479(1)	113.887(1)
γ [°]	65.032(1)	90.000
V [Å^3]	1,090.1(1)	10,639.7(2)
Z	2	8
ρ_{calcd} [g cm^{-3}]	2.139	1.883
dimensions [mm]	0.40 × 0.20 × 0.18	0.30 × 0.38 × 0.40
μ [cm^{-1}]	3.19	2.70
$F(000)$	680	5904
θ range [°]	1.80 to 28.30	1.41 to 28.30
index range	$-11 \leq h \leq 13$	$-19 \leq h \leq 19$
	$-14 \leq k \leq 13$	$-64 \leq k \leq 64$
	$-14 \leq l \leq 15$	$-21 \leq l \leq 21$
reflections collected	7230	67198
independent reflections	4997	25205
refinement method	[b]	[b]
data/restraints/parameters	4997/0/380	25205/0/1640
goodness-of-fit on F^2	1.019	0.955
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0520$	$R_1 = 0.0977$
	$wR_2 = 0.1213$	$wR_2 = 0.1595$
R indices (all data)	$R_1 = 0.0822$	$R_1 = 0.3223$
	$wR_2 = 0.1413$	$wR_2 = 0.2387$
extinction coefficient	0.003(1)	0.00000(5)
largest difference peak/hole [e Å^3]	0.408/ − 0.427	0.355/ − 0.302

[a] $EMI^+ = 1\text{-Et-3-Me-1,3-}C_3H_3N_2^+$. [b] Full-matrix least-squares on F^2.

Table 3. Selected bond lengths [Å] and angles [°]for one of the two nearly identical $Li\{Al(hfip)_4\}_2^-$ ions in the structure of $[EMI][Li\{Al(hfip)_4\}_2]$.[a]

Li1–O1	2.06(1)	Li1–O2	2.05(1)
Li1–O5	2.04(1)	Li1–O6	2.02(1)
Li1–F7	2.83(1)	Li1–F1	2.82(1)
Li1–F25	2.80(1)	Li1–F31	2.66(1)
Al1–O1	1.775(4)	Al1–O2	1.774(4)
Al1–O3	1.722(4)	Al1–O4	1.712(5)
Al2–O5	1.763(4)	Al2–O6	1.777(4)
Al2–O7	1.714(4)	Al2–O8	1.722(5)
O1-Li1-O2	78.0(4)	O1-Li1-O5	138.6(6)
O1-Li1-O6	117.8(5)	O2-Li1-O5	112.5(5)
O2-Li1-O6	142.8(6)	O5-Li1-O6	78.8(4)

[a] $EMI^+ = 1\text{-Et-3-Me-1,3-}C_3H_3N_2^+$, $HFIP = OCH(CF_3)_2$.

Results and Discussion

pK_a values of the HOR_F polyfluoroalcohols: As discussed in the Experimental Section, the aqueous pK_a values of H(HFIP), H(HFTB), and H(PFTB) were known. We determined the aqueous pK_a values of H(HFPP) and H(HFCP) for the first time. We determined the 60:40 (v/v) $DMSO/H_2O$ pK_a value of H(HFBuPP) for the first time and derived the aqueous pK_a of this alcohol using the graph shown in Figure 1. We could not determine the pK_a value of H(DPTE) in either solvent system. However, we can estimate its aqueous pK_a value by assuming the linearity of substituent effects in two different series of fluoroalcohols. In the first series, the CF_3/Ph substitution H(PFTB) → H(HFPP) changes the aqueous pK_a from 5.4 to 8.8, a change of +3.4 pK_a units. Therefore, the second CF_3/Ph substitution H(HFPP) → H(DPTE) should change the pK_a again by +3.4 units, from 8.8 to 12.2. In the second series, the H/Ph substitution H(HFIP) → H(HFPP) changes the pK_a from 9.3 to 8.8, a change of −0.5 pK_a units. Therefore, the double 2H/2Ph substitution $HOCH_2CF_3$ (pK_a = 12.8[14]) → H(DPTE) should change the pK_a by −1.0 units, from 12.8 to 11.8. As a result of this substituent analysis, we estimate the aqueous pK_a value of H(DPTE) to be ~12.

Table 4. Selected bond lengths [Å] and angles [°] for $LiAl(hfip)_4$.[a]

Li–O1	2.089(5)	Li–O2	2.166(6)
Li–O2′	2.533(6)	Li–O4′	2.016(5)
Li–F1	3.327(6)	Li–F3	2.366(6)
Li–F11	3.055(6)	Li–F9′	2.414(6)
Li–F19′	3.181(6)	Li–F20′	2.798(6)
Al–O1	1.758(2)	Al–O2	1.771(2)
Al–O3	1.690(2)	Al–O4	1.766(2)
O3-Al-O1	111.1(1)	O3-Al-O4	112.1(1)
O1-Al-O4	112.41(9)	O3-Al-O2	127.1(1)
O1-Al-O2	94.49(9)	O4-Al-O2	98.17(9)
O1-Li-O2	75.0(2)	O1-Li-O2′	89.9(3)
O1-Li-O4′	160.4(3)	O2-Li-O2′	82.0(3)
O2-Li-O4′	97.5(2)	O2′-Li-O4′	146.8(3)
F1-Li-F3	39.9(3)	F1-Li-F11	56.5(3)
F1-Li-F9′	113.4(3)	F1-Li-F19′	102.5(3)
F1-Li-F20′	77.5(3)	F3-Li-F11	82.5(3)
F3-Li-F9′	79.2(3)	F3-Li-F19′	68.8(3)
F3-Li-F20′	64.7(3)	F11-Li-F9′	157.2(3)
F11-Li-F19′	97.2(3)	F11-Li-F20′	56.4(3)
F9′-Li-F19′	63.4(3)	F9′-Li-F20′	103.0(3)
F19′-Li-F20′	40.9(3)		

[a] $HFIP = OCH(CF_3)_2$.

Relative Lewis basicities of $Al(OR_F)_4^-$ ions: One of the most important properties of a superweak anion is its Lewis basicity with respect to the cation of interest. Several methods of measuring or estimating the "coordinating ability" of weakly coordinating anions have been proposed.[2, 3] Most, if not all, of these methods have limitations.[3] One of the most evident limitations is the choice of reference cationic Lewis acid (LA^+), because each Lewis acid has a unique set of steric and electronic properties that govern the position of the equilibrium shown in Equation (1) (X^- and Y^- are two anions whose Lewis basicities are being compared).

$$LA{-}X + Y^- \rightleftharpoons LA{-}Y + X^- \qquad (1)$$

We chose Li^+ as the reference Lewis acid for this study because it is the next most sterically innocent Lewis acid cation after H^+ and because it forms stable, multidentate complexes with $Al(OR_F)_4^-$ ions in low dielectric solvents, in which the Li^+ cation coordinates to two polyfluoroalkoxide oxygen atoms and to a number of fluorine atoms,[4, 6–10] as shown in Figure 2 for $LiAl(hfpp)_4$.[7, 10] This was essential because we wanted to measure the relative Lewis basicities of $Al(OR_F)_4^-$ ions at their most basic sites, their four oxygen atoms. Subsequent studies from our laboratory will examine sterically more demanding Lewis acid cations, which might only be able to coordinate to the fluorine atoms or other substituents on the periphery of the anions.

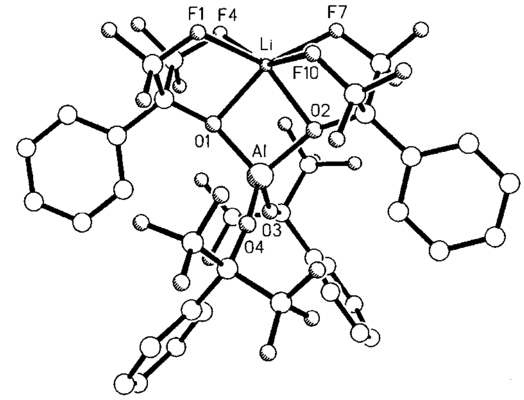


Figure 2. Structure of $LiAl\{OCPh(CF_3)_2\}_4$, showing the trigonal-prismatic LiO_2F_4 coordination sphere. The unlabeled open spheres are carbon atoms and the unlabeled highlighted spheres are fluorine atoms. Hydrogen atoms have been omitted for clarity.

We chose $N(nBu)_4^+$ salts of the $Al(OR_F)_4^-$ ions as the source of "free" $Al(OR_F)_4^-$ and [D$_2$]dichloromethane as the solvent because it has an optimum combination of low dielectric constant (9.1 at 20 °C) and low donor number (~ 0).[20] The version of the generic equilibrium [i.e., Eq. (1)] that was used for this study is given in Equation (2).

$$LiAl(hfpp)_4 + Al(OR_F)_4^- \rightleftharpoons LiAl(OR_F)_4 + Al(hfpp)_4^- \qquad (2)$$

The equilibrium quotient is given by $K = [LiAl(OR_F)_4][Al(hfpp)_4^-]/[LiAl(hfpp)_4][Al(OR_F)_4^-]$ and is defined in this study as the Lewis basicity of $Al(OR_F)_4^-$ relative to $Al(hfpp)_4^-$ with respect to the Lewis acid Li^+. Therefore, a small K value denotes a low Lewis basicity. Note that this definition is based on the assumption that ion pairing interactions between $N(nBu)_4^+$ and the different $Al(OR_F)_4^-$ ions are constant and do not affect the magnitude of K.

We monitored the positions of the equilibria represented above by ^{19}F NMR spectroscopy. It was previously shown that the ^{19}F NMR spectrum of $LiAl(hfpp)_4$ in [D$_{14}$]methylcyclohexane at 25 °C is consistent with a single fluorine-atom environment.[10] This observation, plus the observed average $J(^7Li^{19}F)$ value of 2.4 Hz, indicated a rapid intramolecular exchange of all 24 fluorine atoms under these conditions.[10] We have now found that the fluorine atoms in $LiAl(hfpp)_4$ also exhibit rapid intramolecular exchange in [D$_2$]dichloromethane at 25 °C, although the $J(^7Li^{19}F)$ value was sufficiently small that the 1:1:1:1 quartet was not resolved. However, the width of the ^{19}F resonance became significantly more narrow upon ^7Li decoupling; it changed from 6.35 Hz with no decoupling to 4.95 Hz with broad-band ^7Li decoupling. (In addition, the ^7Li NMR spectrum of $LiAl(hfpp)_4$ in [D$_2$]dichloromethane at 25 °C showed a single resonance, the width of which changed from 12.75 Hz to 5.09 Hz upon broad-band ^{19}F decoupling.) Cooling the solution to -70 °C did not result in a slow-exchange spectrum that would be consistent with a structure similar to that shown in Figure 2. These results, along with the lack of resonances due to free Li^+ or free $Al(hfpp)_4^-$, indicate that the extent of dissociation of $LiAl(hfpp)_4$ into its constituent ions in dichloromethane solution is less than or equal to 1 %. We suspect that the same is true for the other $LiAl(OR_F)_4$ compounds used in this study.

In contrast to the lack of intermolecular exchange of Li^+ and $Al(hfpp)_4^-$ ions solution of $LiAl(hfpp)_4$ in dichloromethane, the ^{19}F NMR spectrum of an equimolar mixture of $LiAl(hfpp)_4$ and $[N(nBu)_4][Al(hfpp)_4]$ in [D$_2$]dichloromethane at 25 °C revealed rapid intermolecular exchange of free and Li^+-coordinated $Al(hfpp)_4^-$ ions. At this temperature, the mixture exhibited only one resonance, $\delta = -75.00$, which is the average of the δ values for the individual compounds (see Table 1). When the sample was cooled to -70 °C, two signals for the individual compounds were observed, as shown in Figure 3 (the δ values for individual samples of $LiAl(hfpp)_4$

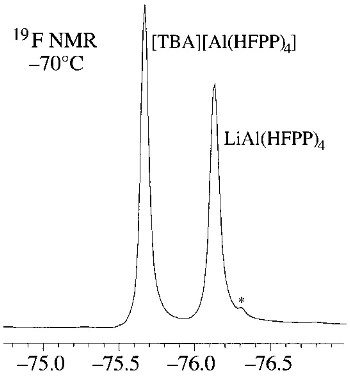
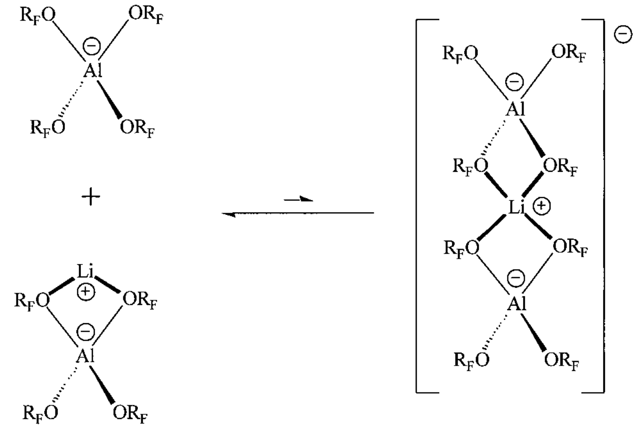


Figure 3. ^{19}F NMR spectrum (CD_2Cl_2) of an equimolar mixture of $LiAl(hfpp)_4$ and $[N(nBu)_4][Al(hfpp)_4]$ at -70 °C. Note that the linewidth of the $LiAl(hfpp)_4$ resonance is slightly larger than for the $[N(nBu)_4][Al(hfpp)_4]$ resonance. The small peak marked with an asterisk is an impurity.

and $[N(nBu)_4][Al(hfpp)_4]$ at −70 °C are −76.12 and −75.70, respectively). Since any dissociation of $LiAl(hfpp)_4$ into free ions at 25 °C is much slower than the exchange rate observed for the mixture at 25 °C, we propose that the exchange of free and coordinated $Al(hfpp)_4^-$ ions occurs by an associative mechanism such as the one shown in Scheme 1. As will be discussed below, the proposed $Li(Al(OR_F)_4)_2^-$ intermediate was observed in solution and isolated in the solid state in the case of $OR_F = HFIP$.



Scheme 1. Proposed mechanism of exchange of free and Li^+-coordinated $Al(OR_F)_4^-$ ions in dichloromethane solution. The idealized symmetry of the $Li(Al(OR_F)_4)_2^-$ ion is D_{2h} or D_{2d}.

A typical Lewis basicity determination consisted of examining the ^{19}F NMR spectrum of an equimolar mixture of $LiAl(hfpp)_4$ and the $N(nBu)_4^+$ salt of a different $Al(OR_F)_4^-$ ion in [D$_2$]dichloromethane at 25 °C. Due to the rapid intermolecular exchange, only two ^{19}F signals were observed for the four species involved in the equilibrium shown in Equation (2), one signal for free and coordinated $Al(hfpp)_4^-$ and one signal for free and coordinated $Al(OR_F)_4^-$. The equilibrium quotient, K, was determined from the δ values of the two observed resonances using Equations (3) and (4),[21] in which N is the mole fraction of the indicated species.

$$\delta(\mathrm{hfpp})_{\mathrm{obs}} = N(\mathrm{Al(hfpp)_4^-})\,\delta(\mathrm{Al(OR_F)_4^-}) + N(\mathrm{LiAl(OR_F)_4})\,\delta(\mathrm{LiAl(OR_F)_4}) \quad (3)$$

$$\delta(\mathrm{OR_F})_{\mathrm{obs}} = N(\mathrm{Al(OR_F)_4^-})\,\delta(\mathrm{Al(OR_F)_4^-}) + N(\mathrm{LiAl(OR_F)_4})\,\delta(\mathrm{LiAl(OR_F)_4}) \quad (4)$$

In some cases, mixtures of $[N(nBu)_4][Al(hfpp)_4]$ and $LiAl(OR_F)_4$ were also studied so that the equilibrium would be approached from the other direction. The same K values were observed regardless of the direction of the approach to equilibrium. When the ^{19}F δ value of a particular $Al(OR_F)_4^-$ ion was close to that of $Al(hfpp)_4^-$, a different mixture of compounds was used and K values were determined from ratios of the measured equilibrium quotients.

The K values (i.e., the relative Lewis basicities) for six of the seven $Al(OR_F)_4^-$ ions examined in this study were determined in this manner. For $Al(pftb)_4^-$ and $Al(dpte)_4^-$, the equilibria represented by Equation (2) were so far to the left and right, respectively, that only upper and lower limits for K of 0.001 and 1000, respectively, could be determined. For reasons that will be discussed in the next section, the K value for $Al(hfip)_4^-$ could not be determined. The six K values are listed in Table 5, which also lists the aqueous pK_a values of the corresponding fluoroalcohols, the formula-unit volumes of four of the seven $LiAl(OR_F)_4$ compounds, and the conductivities of the seven $LiAl(OR_F)_4$ compounds in acetonitrile. There is no correlation between K and the formula-unit volume (i.e., between K and the size of the $Al(OR_F)_4^-$ ion). However, there is a strong, nearly linear correlation between K and the Brønsted basicity of the corresponding OR_F^- alkoxide ion, as shown in Figure 4. The order of increasing Lewis basicity is $Al(pftb)_4^- < Al(hfpp)_4^- < Al(hfBupp)_4^- \sim Al(hftb)_4^- < Al(hfcp)_4^- < Al(dpte)_4^-$. These results indicate that the relative Lewis basicities of these six $Al(OR_F)_4^-$ for

Table 5. Equilibrium quotients, pK_a values, formula unit volumes, and conductivites.

OR_F[a]	K[b]	pK_a of HOR_F[c]	Formula unit volume of $LiAl(OR_F)_4$ [Å][d]	Conductivity of $LiAl(OR_F)_4$ [mS cm^{-1}][e]
PFTB	≤ 0.001	5.4		0.927
HFPP	1	8.8	977.0	0.883
HFBuPP	11	9.3		0.786
HFTB	17	9.6		1.02
HFCP	50	10.3	1047	0.883
DPTE	$\geq 1 \times 10^3$	~12	1196	0.750
HFIP		9.3	545.0	1.02
TFE		12.8		

[a] $PFTB = OC(CF_3)_3$, $HFPP = OCPh(CF_3)_2$, $HFBuPP = OC\{4\text{-}C_6H_4\text{-}(t\mathrm{Bu})\}(CF_3)_2$, $HFTB = OC(CH_3)(CF_3)_2$, $HFCP = OC(Cy)(CF_3)_2$, $DPTE = OCPh_2(CF_3)$, $HFIP = OCH(CF_3)_2$, $TFE = OCH_2CF_3$. [b] Equilibrium quotient for the reaction of $LiAl(hfpp)_4 + Al(ORF)_4^- \rightleftharpoons LiAl(OR_F)^4 + Al(hfpp)_4^-$ ([D$_2$]dichloromethane, 25 °C). [c] Aqueous pK_a value. [d] From X.ray structure determinations. [e] Conductivity of solutions in acetonitrile (0.01 M).

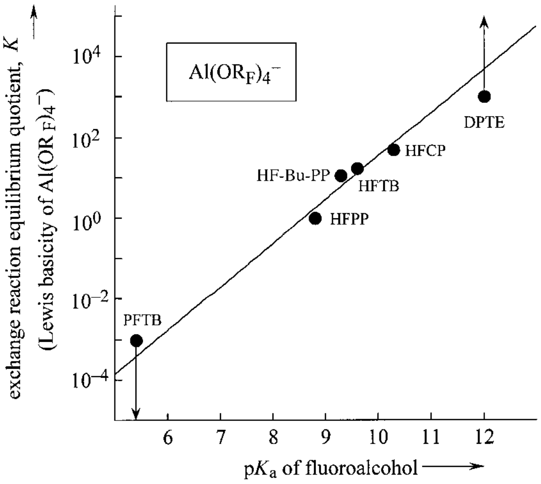


Figure 4. Plot of log K for the exchange reaction $LiAl(hfpp)_4 + Al(OR_F)_4^- \rightleftharpoons LiAl(OR_F)_4 + Al(hfpp)_4^-$ versus aqueous pK_a value for the corresponding parent fluoroalcohol. The log K values for $Al(pftb)_4^-$ and $Al(dpte)_4^-$ represent upper and lower limits, respectively. The straight line is a linear least-squares fit to the four central data points. Note that log K is defined as 0 for the $Al(hfpp)_4^-$ ion.

Li^+ in dichloromethane depend only on the corresponding Brønsted basicities of the parent fluoroalkoxides and not on the steric properties of the various substituents on the fluoroalkoxides. In an important related study, Krossing proved that the $Al(pftb)_4^-$ ion is a weaker Lewis base than the $Al(hfip)_4^-$ ion for Ag^+ by showing that the equilibrium in Equation (5) lies to the right for $Al(hfip)_4^-$ but lies to the left for $Al(pftb)_4^-$ ($L = 1,2\text{-}C_2H_4Cl_2$).[5]

$$\underset{\text{no Ag–O(Al) bonds}}{\underset{\text{ionic compound}}{[Ag(L)_3]^+[Al(OR_F)_4]^-(s)}} \rightleftharpoons \underset{\text{two Ag–O bonds}}{\underset{\text{molecular compound}}{[Ag(L)_2\{Al(OR_F)_4\}](s)}} + L(l) \qquad (5)$$

On the basis of an analysis of ^{27}Al NMR line widths, Krossing also concluded that the order of basicity towards either Ag^+ or Li^+ in [D]chloroform is $Al(pftb)_4^- < Al(hfip)_4^- < Al(hftb)_4^-$.[5]

The conductivites of solutions of the seven $LiAl(OR_F)_4$ compounds in acetonitrile (0.01M) are listed in Table 5. There is no correlation between anion basicity in dichloromethane and Li^+ salt conductivity in acetonitrile (ACN). The equilibria that govern conductivity are given in Equation (6) (all species are solvated by acetonitrile, ACN).

$$LiAl(OR_F)_4 \xrightleftharpoons{ACN} [Li(ACN)_4Al(OR_F)_4] \xrightleftharpoons{ACN} Li(ACN)_4^+ + Al(OR_F)_4^- \qquad (6)$$

The coordinating ability of $Al(OR_F)_4^-$ (i.e., the Lewis basicity of $Al(OR_F)_4^-$) only affects the position of the first equilibrium in Equation (6); the position of the second equilibrium is related to the ion pairing ability of $Al(OR_F)_4^-$, not its coordinating ability. In addition, conductivity depends on cation and anion mobilities and on solution viscosity, which almost certainly vary as a function of the aluminate R_F groups, because these groups have very different sizes. Therefore, we conclude that the measurement of solution conductivities of simple salts of weakly coordinating anions is an imperfect way to gauge the relative Lewis basicities of anions.

The $Li\{Al(hfip)_4\}_2^-$ aggregate ion: It was not possible to determine the Lewis basicity of $Al(hfip)_4^-$ by the ^{19}F NMR procedure described above. The ^{19}F NMR δ value of the exchange-averaged resonance was not the simple mole-fraction-weighted average of the δ values for $LiAl(hfip)_4$ and $[N(nBu)_4][Al(hfip)_4]$, in contrast to the behavior of mixtures of the other $Al(OR_F)_4^-$ compounds. Instead of decreasing monotonically from δ −76.93 to δ −77.26, the observed δ value first increased until the mole ratio of the two compounds was ~0.8 and then decreased, as shown in Figure 5. In addition, the ^7Li NMR resonance for mixtures of $LiAl(hfip)_4$ and $[N(nBu)_4][Al(hfip)_4]$ did not have the same δ value as the compound $LiAl(hfip)_4$ itself, again in contrast to the behavior of mixtures of the other $Al(OR_F)_4^-$ compounds. Furthermore, the ^7Li NMR δ value changed when the ratio of the two compounds was changed.

The NMR behavior described above requires the formation of at least one new complex containing the $Al(hfip)_4^-$ ion which has a ^{19}F NMR δ value more positive than −76.93. Since the oxygen atoms in the $Al(hfip)_4^-$ ion should be sterically more accessible than the oxygen atoms of the six other $Al(OR_F)_4^-$ ions, we propose that the new species formed in solution is the $Li\{Al(hfip)_4\}_2^-$ aggregate ion. This ion has the same composition as the proposed intermediate for associative exchange of $Al(OR_F)_4^-$ ions depicted in Scheme 1. The important difference is that the concentration of $Li\{Al(hfip)_4\}_2^-$ is significant when equimolar amounts of $LiAl(hfip)_4$ and $[N(nBu)_4][Al(hfip)_4]$ are present in dichloromethane, whereas the concentrations of the other six $Li\{Al(OR_F)_4\}_2^-$ aggregate ions are so low that they cannot be detected by NMR spectroscopy. A similar aggregated species with a $Li\{Al(hfip)_4\}_2^-$ core was proposed by Krossing to explain variable-temperature ^7Li NMR results for $LiAl(hfip)_4$ dissolved in [D]chloroform containing diethyl ether.[5]

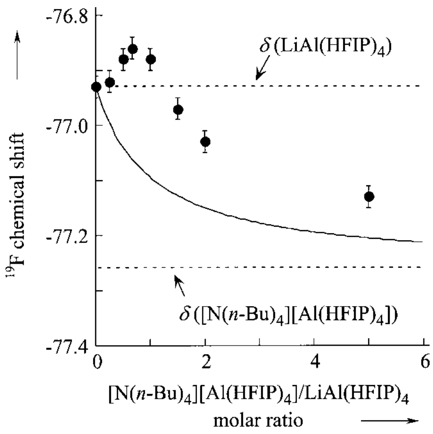


Figure 5. ^{19}F NMR δ value (CD_2Cl_2, 25 °C) versus $[N(n\text{-}Bu)_4][Al(hfip)_4]/LiAl(hfip)_4$ mole ratio for mixtures of $[N(nBu)_4][Al(hfip)_4]$ and $LiAl(hfip)_4$. The curve is the weighted-average δ value for these two compounds versus the mole ratio. The data clearly indicate that at least one new HFIP-containing species has formed and is in rapid exchange with both $LiAl(hfip)_4$ and the free $Al(hfip)_4^-$ ion.

We isolated the $Li\{Al(hfip)_4\}_2^-$ aggregate ion in the solid state as its EMI^+ salt. The structure of one of the two nearly identical anions is shown in Figure 6 (the structures of the two nearly identical cations are normal). Selected bond lengths and angles are listed in Table 3. The structure of the anion, which has no crystallographic symmetry but which has idealized D_{2d} symmetry, consists of a central Li^+ cation bonded to four oxygen atoms, two from each of its $Al(hfip)_4^-$ ions. The Al1-Li1-Al2 angle is greater than 174°. The Li^+ cation is also bonded to four fluorine atoms, each one from four different CF_3 groups, forming five-membered Li-F-C-C-O chelate rings.

Each of the two $Al(hfip)_4^-$ ions in the aggregate anion complex acts as a tetradentate O_2F_2 chelating ligand. The Li1–O bond lengths range from 2.03(1) to 2.05(1) Å. The Li1–F bond lengths are more than 30% longer and range from 2.77(2) to 2.82(2) Å. The next shortest Li–F contact is > 3.5 Å. The LiO_4F_4 coordination sphere for Li1, two views of which are shown in Figure 6, can be described as a distorted square antiprism, which is a common geometry for eight-coordinate Li^+ ions.[22] The O1-F1-O6-F31 and O2-F7-O5-F25 least-squares planes are coplanar to within 0.11 Å. The dihedral angle between these two planes is only 1°. The Li1 atom is 1.16 Å from the centroid of the former plane and

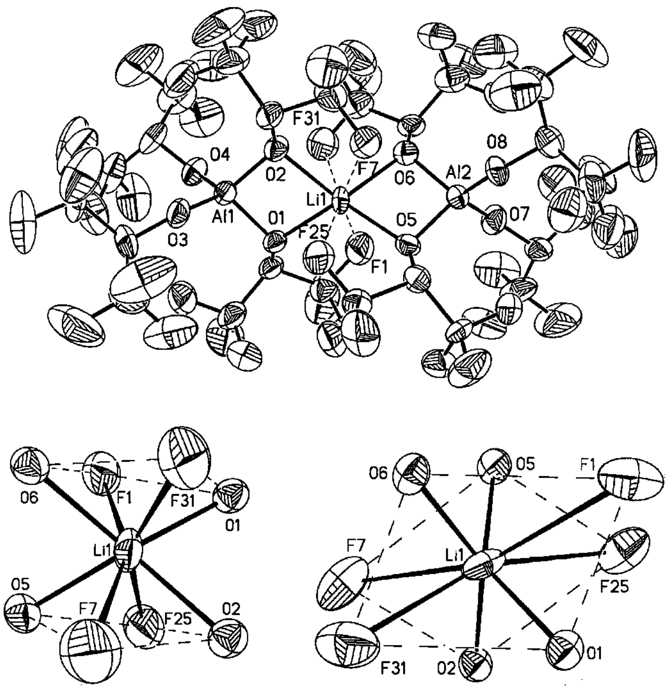


Figure 6. Drawing of one of the two nearly identical $Li(Al(hfip)_4)_2^-$ ions in the structure of $[EMI][Li\{Al\{OCH(CF_3)_2\}_4\}_2]$ and two views of the LiO_4F_4 coordination sphere (50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (Å): Li1–O1, 2.06(1); Li1–O2, 2.05(1); Li1–O5, 2.04(1); Li1–O6, 2.02(1); Li1–F7,2.83(1); Li1–F1, 2.82(1); Li1–F25, 2.80(1); Li1–F31, 2.66(1).

1.23 Å from the centroid of the latter plane. The centroid-Li1-centroid angle is 176°.

The four Li–F bonds in each $Li\{Al(hfip)_4\}_2^-$ ion, although clearly weaker than the four Li–O bonds, are still significant as far as the sums of the lithium bond valences for the two $Li\{Al(hfip)_4\}_2^-$ ions, 1.00 ± 0.01, is concerned (since the valence of lithium is $+1$, the sum of lithium bond valences should be within a few percent of 1.00).[23] The sum of the Li–F bond valences is 20% of the total in each of the two $Li\{Al(hfip)_4\}_2^-$ ions (tables of bond valences for the compounds discussed in this paper are given in the Supporting Information). There are no fluorine atoms in the structure of $LiNb(OEt)_6$, which contains four Li–O bonds in a D_{2d}-distorted tetrahedral array and with an average Li–O bond length of 1.94(3) Å.[24] There are no other bonds to the Li^+ ion. In this case, the four Li–O bonds are shorter than the four Li–O bonds in $Li\{Al(hfip)_4\}_2^-$ and, not surprisingly, the sum of Li–O bond valences in $LiNb(OEt)_6$ is 0.98. In the recent report of the structure of the related anionic species $Li\{Nb(OC_6F_5)_6\}_2^-$,[11] the authors described the lithium coordination sphere as square-planar, which, if true, would be unique for a LiO_4 coordination unit.[22] We have found that the sum of the four Li–O bond valences for $Li\{Nb(OC_6F_5)_6\}_2^-$ is only 0.80. Therefore, we suspect that the $Li\{Nb(OC_6F_5)_6\}_2^-$ ion also contains Li–F interactions not mentioned by the authors. An analysis of their structural results revealed four such Li–F interactions, two at 2.614(4) Å and two at 3.159(4) Å, giving a sum of Li–F bond valences of 0.19 and a total lithium bond valence sum of 0.99 (the sum of van der Waals radii for lithium and fluorine is ~3.3 Å[25]). Therefore, the lithium coordination sphere in $Li\{Nb(OC_6F_5)_6\}_2^-$ is best represented as LiO_4F_4, the same as in the $Li\{Al(hfip)_4\}_2^-$ ion.

Structure of $LiAl(hfip)_4$: In related work that has been or that will be published elsewhere, we have determined the structures of $LiAl(hfpp)_4$,[7, 10] $LiAl(hfcp)_4$,[9] $LiAl(dpte)_4$,[9] and $LiAl\{OC(4-C_5H_4CH_3)(CF_3)_2\}_4$.[8] Each of these compounds has two, and only two, Li–O(Al) bonds in addition to a number of longer, but important, Li–F bonds. The structure of the $Li\{Al(hfip)_4\}_2^-$ ion suggested that a different structural motif might be possible for $LiAl(hfip)_4$, and we have now found this to be the case. The structure of $LiAl(hfip)_4$ is shown in Figure 7. Selected bond lengths and angles are listed in Table 4. The structure of this compound consists of centrosymmetric dinuclear molecules composed of two Li^+ and two tetrahedral $Al(hfip)_4^-$ ions. Each $Al(hfip)_4^-$ ion donates three of its four oxygen atoms to the Li^+ cations, one each to the two Li^+ cations and a third that bridges the two Li^+ cations forming a planar Li_2O_2 core. Each Li^+ cation is also bonded to six fluorine atoms from four different CF_3 groups. The sums of Li–O and Li–F bond valences are 0.64 and 0.32, respectively. Therefore, the Li–F bond valences contribute 33% of the total lithium bond valence sum, which is 0.96. As expected, the AlO_4 core is distorted from a tetrahedral geometry. Since O3 does not bond to the Li^+ ions, the Al–O3 bond length, 1.690(2) Å, is considerably shorter than the other three Al–O

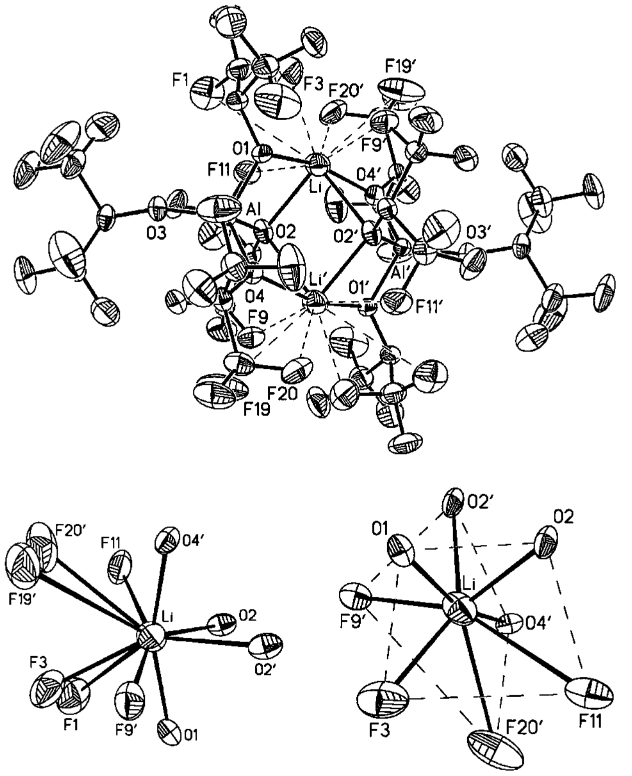


Figure 7. Drawing of the centrosymmetric $[\{LiAl\{OCH(CF_3)_2\}_4\}_2]$ dimer in the structure of $LiAl\{OCH(CF_3)_2\}_4$ and two views of the lithium coordination sphere (50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (Å): Li–O1, 2.089(5); Li–O2, 2.166(6); Li–O2′, 2.533(6); Li–O4′, 2.016(5); Li–F1, 3.327(6); Li–F3, 2.366(6); Li–F11, 3.055(6); Li–F9′, 2.414(6); Li–F19′, 3.181(6); Li–F20′, 2.798(6).

bonds, which range from 1.758(2) to 1.771(2) Å. The O1-Al-O2 and O2-Al-O4 bond angles are 94.49(9) and 98.17(9)°. The other four O-Al-O angles range from 111.1(1) to 127.0(1)°. The LiO_4F_6 coordination sphere, shown in Figure 7, is much less symmetric than the LiO_4F_4 coordination spheres in the $Li\{Al(hfip)_4\}_2^-$ and $Li\{Nb(OC_6F_5)_6\}_2^-$ ions. The four oxygen ligands occupy one hemisphere and the six fluorine ligands occupy the other hemisphere. The Li−O1, Li−O2, Li−O2′, and Li−O4′ bond lengths are 2.089(5), 2.166(6), 2.533(6), and 2.016(5) Å, respectively. The Li−F bond lengths range from 2.366(6) to 3.327(6) Å (the next shortest Li−F length is >3.5 Å). Ignoring the two longest Li−F bonds, each of which has a bond valence of less than 3% of the total, the remaining LiO_4F_4 coordination sphere can be described as a highly distorted square antiprism. A view of the truncated LiO_4F_4 coordination sphere is also shown in Figure 7. The four-atom least-squares planes indicated by the dashed lines in Figure 7 are much less planar than in the $Li\{Al(hfip)_4\}_2^-$ ion, and the two planes make a dihedral angle of 15°. By comparing the lower-right drawings in Figure 6 and Figure 7, one can clearly envision that the hypothetical transformation $2[LiAl(hfip)_4]_2(s) + EMI^+(g) \rightarrow [EMI][Li\{Al(hfip)_4\}_2](s) + Li^+(g)$ would require only a modest amount of coordination-sphere rearrangement around the remaining Li^+ ion. Furthermore, by comparing the upper drawings in Figure 6 and Figure 7, one can understand why these structures would be destabilized if the HFIP substituents were exchanged for any of the other, sterically more demanding, OR_F substituents.

Acknowledgement

This research was supported U.S. National Science Foundation grants CHE-9628769 and CHE-9905482. We also thank Central Glass Company for financial support and the NIH Shared Instrumentation Grant Program for the SMART X-ray system.

---

[1] The term "superweak anion" is used to draw attention to the conceptual connection between very weakly coordinating anions and superacid media, because both involve the virtual absence of basicity. Specifically, a superweak anion is the conjugate base of a superacid. We also use the term for an extremely weakly coordinating anion whose conjugate acid is unknown or has not yet been shown to be a superacid.

[2] a) A. J. Lupinetti, S. H. Strauss, *Chemtracts: Inorg. Chem.* **1998**, *11*, 565; b) "Superacids and Super Anions", C. A. Reed, N. L. P. Fackler, T. Drovetskaya, D. R. Evans, *Abstracts of Papers*, 215th ACS National Meeting, Dallas, TX, **1998**, Abstract INOR 202; c) "New Weakly Coordinating Anions $CB_{11}H_{12-n}F_n^-$, $CB_9H_{10-n}F_n^-$, and $Al(OR_F)_4^-$: Is Perfluorination Achievable, and, If So, Is It Desirable", S. H. Strauss, *Abstracts of Papers*, 215th ACS National Meeting, Dallas, TX, **1998**, Abstract INOR 404.

[3] a) E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391; b) C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 133; c) A. R. Siedle, B. Hanggi, R. A. Newmark, K. R. Mann, T. Wilson, *Makromol. Chem. Macromol. Symp.* **1995**, *89*, 299; d) S. H. Strauss, *Chemtracts: Inorg. Chem.* **1994**, *6*, 1; e) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927; f) M. Bochmann, *Angew. Chem.* **1992**, *104*, 1206; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1181.

[4] T. J. Barbarich, Ph.D. Dissertation, Colorado State University, **1999**.

[5] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490.

[6] "Fluorocarboranes and Fluoroalkoxyborates and -Aluminates", S. H. Strauss, *Abstracts of Papers*, 218th ACS National Meeting, New Orleans, LA, **1999**, Abstract FLUO 1.

[7] T. J. Barbarich, S. M. Miller, O. P. Anderson, S. H. Strauss, *J. Mol. Catal.* **1998**, *128*, 289.

[8] S. Tsujioka, B. G. Nolan, T. J. Barbarich, S. M. Ivanova, B. P. Fauber, J. C. Brady, C. E. Kriley, S. M. Miller, O. P. Anderson, A. Bell, S. H. Strauss, unpublished results.

[9] T. J. Barbarich, B. G. Nolan, S. M. Ivanova, S. Tsujioka, S. M. Miller, O. P. Anderson, and S. H. Strauss, unpublished results.

[10] T. J. Barbarich, S. T. Handy, S. M. Miller, O. P. Anderson, P. A. Grieco, S. H. Strauss, *Organometallics* **1996**, *15*, 3776.

[11] Y. Sun, M. V. Metz, C. L. Stern, T. J. Marks, *Organometallics* **2000**, *19*, 1625.

[12] J. J. Rockwell, G. M. Kloster, W. J. Dubay, P. A. Grieco, D. F. Shriver, S. H. Strauss, *Inorg. Chim. Acta* **1997**, *263*, 195.

[13] B. G. Nolan, S. Tsujioka, B. P. Fauber, S. H. Strauss, unpublished results.

[14] a) B. L. Dyatkin, E. P. Mochalina, I. L. Knunyants, *Tetrahedron* **1965**, *21*, 2991; b) C. J. Willis, *Coord. Chem. Rev.* **1988**, *88*, 133.

[15] J. R. Gandler, W. P. Jencks, *J. Am. Chem. Soc.* **1982**, *104*, 1937.

[16] G. M. Sheldrick, *SMART/SAINT*, Siemens Analytical X-Ray Instruments, Madison, WI, **1994**.

[17] G. M. Sheldrick, *SHELXTL*, version 5.03 **1994**.

[18] H. D. Flack, *Acta Crystallogr. Sect. A* **1989**, *39*, 876.

[19] G. Bernardinelli, H. D. Flack, *Acta Crystallogr. Sect. A* **1985**, *41*, 500.

[20] a) V. Gutmann, *Coord. Chem. Rev.* **1967**, *2*, 239; b) V. Gutmann, *Coordination Chemistry in Non-aqueous Solvents*, Springer, Wien/New York, **1969**; c) V. Gutmann, *Coord. Chem. Rev.* **1976**, *18*, 225.

[21] F. L. Slejko, R. S. Drago, D. G. Brown, *J. Am. Chem. Soc.* **1972**, *94*, 9210.

[22] U. Olsher, R. M. Izatt, J. S. Bradshaw, N. K. Dalley, *Chem. Rev.* **1991**, *91*, 137.

[23] a) I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244; b) M. O'Keefe, *Struct. Bonding*, **1989**, *71*, 161; c) J. A. Samuels, E. B. Lobkovsky, W. E. Streib, K. Folting, J. C. Huffman, J. W. Zwanziger, K. G. Caulton, *J. Am. Chem. Soc.* **1993**, *115*, 5093.

[24] D. J. Eichorst, D. A. Payne, S. R. Wilson, K. E. Howard, *Inorg. Chem.* **1990**, *29*, 1458.

[25] a) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, **1960**; b) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

Received: June 6, 2000 [F2528]